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Method and System for Processing Carrier Materials by Heavy Ion Irradiation and Subsequent Etching

BACKGROUND OF THE INVENTION.

1. Field of the Invention.

The invention relates to a method and to a system for processing a dielectric carrier material by heavy ion irradiation and subsequent etching which make it possible to emboss a surface depth relief into the carrier material which forms the basis for passive or active layers connectively applied to the carrier material.

2. The Prior Art.

It is known that when irradiating dielectric materials (polymers, glasses, etc.) with high-energy heavy ions so-called latent traces" of a diameter in the nanometer range (10 to several 10 nm) are created in these materials along the trajectories of the ions moving through the material as a result of energy dissipation by radiation interactions and subsequent secondary reactions. The length of these traces is a function of the influx energy of the ions. Within these latent traces, the material is modified by the radiation and possesses physical and chemical properties different from those of the surrounding dielectric material. It is thus possible by suitable subsequent processes, usually be by chemical etching, to remove the radiation-modified material along the latent traces and in this manner to form so-called "recesses" such as, for instance, etch pits or channel-like structures of various configurations. Etch pits result if the bombarding energy is insufficient to permeate the irradiated material; however, if the energy is sufficient, so-called "micro-channels" are formed. In addition to such irradiation parameters as type of ion, influx energy, irradiation angle, target material (composition and

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structure of the irradiated medium), the shape of the recesses formed is dependent upon the etching rate of the unchanged material (material etching rate v_B and of the modified material in the latent ion trace (trace etching rate v_g). These two parameters may be varied by the selected etching agent, its concentration and temperature. Since aside from the irradiation conditions the material etching rate v_B may additionally be varied by sensitizing (UV-irradiation prior to etching, effect of oxygen, effects of solvents), purpose-related processing of the material may be carried out by the selection of conditions relating to irradiation, etching and, optionally, sensitization.

Aside from usage in dosimetry (where the number of etching pits formed is considered to be a measure of the applied irradiation dose) further technically relevant applications are known based on the described methods of irradiation and subsequent etching.

In the fabrication of ion trace membranes for filtering purposes, polymeric ~~foils~~ films made, for instance, of polyester or polyimide are irradiated by heavy ions such that the ions impinge vertically upon the surface of the ~~foil~~ film. The bombardment energy selected must ensure complete permeation of the ~~foil~~ film, and the energy transfer per length of path (dE/dx) should be as constant as possible ~~during~~ over the entire ion trajectory. The follow-up etching process is optimized such that the resultant recesses are shaped in the manner of cylindrical channels of defined diameter. As a result of ~~the~~ their exact cylindrical shape the channels of the filtering membrane do not become ~~plugged-up~~ congested when used and after back flushing of the filtered residue the initial filtering rate is ~~achieved again~~ restored. The setting of a defined size of pores makes it possible to fabricate ion trace membranes for different fields of application (as bacteria filters, for clarifying processes, etc.). European Patent specification No. EP 0,583,605 Al discloses a method of fabricating such micro-pores by etching particle traces.

The publications DE 2,916,006 Al and EP 0,583,605 Al disclose the

combination of heavy ion irradiation, subsequent etching and subsequent coating of the support surface. They disclose the following method steps for fabricating adherent metal layers on dielectric media without ~~bonding~~ intermediate bonding layers: Irradiation of different dielectric media by heavy ions (mass > 10 and bombardment energy > .1 MeV/amu), especially at an oblique impinging direction of the radiation up to achieving a non-defined fluence. The subsequent etching is carried out until the pits have attained a desired size and thus results in a defined surface roughening. What may conveniently be labeled a "zipper-effect" of etched pits extending obliquely into the surface results in ~~increased connection strength of~~ a metal layer subsequently applied by conventional processes being connected to the surface at increased strength. Extensive tests by the inventor have shown that though it is possible under laboratory conditions to fabricate composites of a carrier ~~foil~~ film and metal layer of desired connection strength (≥ .8 N/mm in accordance with DIN), yet they do not stand up to practical demands especially in respect of immunity from the effects of humidity. The reason for this is that ~~under the effect of~~ humidity ~~on~~ affecting the carrier ~~foil~~ film dissolves the "anchoring" between carrier ~~foil~~ film and metal layer ~~is dissolved~~ (humidity-induced glide effects; "barrel soap effect"), so that the stable connection ~~of~~ between the two components as required for practical purposes is possible only in a dry state.

It is also known to fabricate ion trace membranes for a directional current passage. The irradiation of the polymer ~~foils~~ films is carried out in the same manner as in the production of filter membranes. However, the subsequent etching process, which establishes the formation of channels through the ~~foil~~ film, is in this case optimized such that channels of equal shape and size are generated, ~~the~~ a cylindrical configuration being the desirable one. Further process step result in only the formed channels being filled with metal, whereas the remainder of the surface is not ~~being~~ metallized. In this manner, a membrane is created which is electrically conductive only in a direction normal to its surface: These approaches are described in the

publications DE 196 50 881 Al and DE3337049A1.

Furthermore, a method of processing carrier ~~foils~~ films by irradiation with heavy ions is known from DE 100 58 822 Al. This invention aims at improving the strength of the connection ~~strength the~~ between a carrier ~~foils~~ film and ~~a~~ an applied functional layer ~~to be applied~~.

During its irradiation, the material ~~to be irradiated~~ is guided over a roller system including a deflection roller, a feed roller, a take-up roller and two ~~fixing~~ guide rollers. The deflection roller may be vertically adjusted on a rail parallel to the direction of propagation of the ion beam. By means of the vertically adjustable deflection roller and the ~~fixing~~ guide rollers the carrier ~~foils~~ films may be aligned at two different angles relative to the direction of propagation of the ion beams such that the irradiation with the heavy ions generates a surface depth relief of latent ion traces. Material components of the functional layer to be applied extend into the ion traces etched into pits or recesses and thus anchor the functional layer in the carrier ~~foil~~ film.

The process there described constitutes an initial imperfect ~~beginnings of an irradiation of~~ approach to irradiating carrier ~~foils~~ films in which the heavy ions can impinge at different angles of bombardment.

US Patent 4,416,724 discloses a process of enlarging the surface of a non-conductor by irradiation with heavy ions ~~with~~ wherein the ~~generated~~ latent ion traces ~~being~~ generated are widened by an etching process following the irradiation. Irradiation takes place in a vacuum, the beam direction of the collimated heavy ion beam being partially affected by a rotating grid and by a magnetic deflection device. In this manner, the surface of the non-conductor may be enlarged up to 1,000 times the value of its original surface. The radiation energy, the radiation density and the radiation medium are mentioned as parameters for generating a suitable surface porosity.

~~In respect of~~ As regards the scope of ~~their~~ the applicability of their results, the method steps described in connection with the ~~mentioned solutions~~ prior art referred to above are closely limited to the stated goals of their processes. It is not possible with the elements of the prior art to generate a suitable structure (surface depth relief) representing a reliable and stable basis for ~~the application and sufficiently strong and lasting connection strength of useful layers~~ applying layers connected to a substrate with sufficient strength and durability. The known means can only provide for ~~an adhesion~~ connection of such layers on ~~the~~ a support which ~~are~~ is not subject to any special stresses. If, however, the ~~adhering~~ connected layers are subjected to mechanical stresses or humid conditions, for instance, the connection between support and layer will not be a long-wearing one. For this reason, bonding agents are generally used ~~which~~ to improve the ~~connection~~ strength ~~of~~ at which the applied layers are connected to their substrate but which may nevertheless fail under humid conditions, for instance. It is also possible to subject the carrier ~~foils~~ films to mechanical or thermal surface treatments but these would significantly increase the production complexity.

OBJECT OF THE INVENTION.

It is, therefore, an object of the invention to develop an approach which allows processing of carrier ~~foils~~ films such that passive or active layers may be applied in an extremely adhering manner. The technology to be developed is to replace the use of bonding agents and any mechanical or thermal surface treatment during or prior to coating of the carrier foil film.

BRIEF SUMMARY OF THE INVENTION.

In the accomplishment of this object, the invention provides for a ~~method and an arrangement as set forth by the principal characteristics of claims 1 and 9. Improvements of the invention are set forth in the respective appurtenant sib-claims~~ bombardment of a solid material carrier film by high

energy heavy ion irradiation at two different angles and under special controlled conditions, hereafter to be described, so as initially to form in the carrier film intersecting ion traces which by subsequent chemical etching form intersecting channels below the surface of the carrier film for securely anchoring a metal layer precipitated on the surface of the carrier layer.

Other objects will in part be obvious and will in part appear hereinafter.

In the method according to the invention irradiation and etching are always carried out such that recesses (pores and the like) are formed which do not permeate through a carrier ~~foil. This allows formation of~~ film. In this manner a surface structure can be formed which ~~makes a subsequent adhering~~ results in a strongly connected coating ~~possible~~.

In accordance with the invention the heavy ions must penetrate into the carrier material ~~from~~ by way of at least two different impinging angles. ~~The~~ By varying the bombardment energy, the range of the ions, i.e. their depth of penetration, is changed in accordance with requirements ~~by varying the bombardment energy~~. The different directions of irradiation and sufficiently long etching result in reliefs of varying surface depth ~~reliefs~~. "~~Surface depth relief~~ "Reliefs of varying surface depth" connotes that structuring from the surface up to a predetermined depth ~~of~~ in the material results to a certain extent in blurring of the differences between surface and volume in the structured area. The generated relief is reminiscent of a fractal structure characterized by the fractal dimension D ~~of~~ at 2 < 0 < 3, with D increasing from the surface and ~~attains~~ attaining a value of 3 upon reaching the volume no longer affected by the structuring.

The formation of undercut recesses (e.g. truncated shapes and cavities) is particularly advantageous in such fissured structures. To the extent they can be filled by the second component of the composite, the formed undercuttings, generated by the above-described fractal structure,

constitute the basis of a lasting strong ~~adhesion~~ connection of the cover layer.

The intended connection strength is not solely the result of mechanical action ~~only~~, but also of physical forces occurring on the surface such as, for instance, polarization, dipol-dipol-effects, van der Waal forces, etc. While the latter are strongly reduced by the effect of humidity, the mechanically conditioned bonding action remains unchanged.

The ~~lasting connection~~ strength of a lasting connection in the sense described above can be further improved by ~~generating~~ forming recesses with common intersections ~~of recesses~~. "Common intersection" connotes the meeting or crossing of two recesses.

In accordance with the invention, ~~a precondition of this method in this case as well, is~~ the method of forming such intersecting recesses is also preconditioned on irradiation of the carrier material from at least two impinging angles.

The fluence and direction of bombardment of the heavy ions are selected so as to result in ~~generating~~ forming a maximum number of intersecting or meeting units of volume, in the interior of which the generated ion traces will be present. The recesses which are formed by one of the etching processes following the irradiation are provided with so-called common intersections.

In order to attain a maximum of lasting connection strength by common intersections the irradiation parameters need be specially dimensioned. The following five parameters must be taken into consideration:

a) applied ion fluence;
b) impinging angle of the heavy ions on the carrier surface;
c) angle of the different directions of bombardment of the ions

directed against each other;

d) range of radiation in the solid material; and

e) influx energy or energy dissipation per unit length along the trajectories of the high-energy heavy ions penetrating into the solid material.

Especially ~~high values of connection strength~~ strong connections are obtained by selecting the parameters of irradiation and etching such that following the etching process a surface depth relief ~~has been~~ will be formed which in the area near the surface possesses the described fractal surface structure ~~which has already be described~~ and recesses with frequently occurring common intersections in areas removed from the surface.

For industrial applications of the ion trace technology the required high-energy heavy ions are generated by accelerators. As a rule accelerators are designed to provide high-energy heavy ions of discreet energy values. In ~~a~~ normal ~~case~~ circumstances it is thus necessary to use an additional device ~~which is~~ positioned in the beam guide channel of the irradiation apparatus, i.e. ~~ahead of~~ above the carrier material to be irradiated. By means of this device it is possible to adjust the beam to a predetermined energy value ~~which is~~ representative of the influx ~~value~~ power of the ion energy for the solid material to be irradiated (e.g. a polymeric ~~foil~~ film). The device will hereafter be called deceleration module and may consist, for instance, of thin metal ~~foils~~ films. In accordance with the invention the deceleration module is arranged in the direction of the propagation of the heavy ion beams ~~ahead of~~ above the roller system and, therefore, ~~in front of~~ facing the carrier material to be irradiated. The adjustment of the influx ~~energy which has to be less~~ power to a level lower than the energy level of the ions ~~after leaving~~ emitted by the accelerator takes place ~~by~~ when the high-energy heavy ions ~~losing~~ lose energy during their penetration through thin metal foils. Hence, a discrete predetermined influx energy corresponding to the energy level desired for the solid body to be irradiated, can be ~~generated~~ established by selection of the

thickness of the metal foils.

As regards the irradiation technology, there are two possible variants ~~for the realization~~ of practicing the method referred to *supra:*

On the one hand, the influx angle relative to the surfaces and radiation directed against each other is kept constant by appropriate collimation of the impinging radiation from at least two directions so that only fluence and range of the heavy ion radiation need be tuned relative to each other in order to generate a maximum of ~~intersection~~ intersections within a defined area of the carrier material.

On the other hand, no collimation of the heavy ion radiation impinging from at least two directions ~~will be~~ is provided so that as a result of the thus possible variation of the impinging and intersecting angles the formation and distribution of intersections in the carrier material take place substantially stochastically. In that case, all parameters must be included in the optimization which would require a ~~solution~~ model by computer simulation of the process in order to determine the conditions for a maximum value regarding intersections.

The etching conditions of the irradiated material have to be selected to form optimally shaped recesses. In this connection, it is desirable to aim at an aspect ratio A, i.e. the ratio of the length of the pores to the diameter of the pores, of ≥ 3.

The inventive combination of irradiation and etching conditions makes it possible, by way of the method of operation not only to produce undercuttings but also, because of the connected pores present at the intersections, so-called "tie-ins" which ~~guarantee~~ ensure a lasting and strong connection ~~strength~~ of the cover layer of the composite anchored thereto.

The present invention makes possible the fabrication of composites of a carrier material and cover layers without any bonding agent of any kind. The composites are characterized by lasting ~~high values of connection strength~~ and strong connections between substrate and coating, especially under conditions in which they are in contact with water or aqueous solutions or exposed to highly humid atmospheres.

In accordance with the invention the connection strength of applied layers can be further improved by overetching.

A preferred embodiment ~~for~~ of an irradiation device of the novel method is characterized by an ion trace ~~foil~~ film being transported as a carrier ~~foil~~ film over a guide system and being arranged with an adjustable angle of inclination $\pm\alpha_1/\pm\alpha_2$ relative to the impinging ion beams with the edges of the ~~foil~~ film sheet guided at this angle of inclination extending symmetrically or asymmetrically relative to the longitudinal direction of the ion beams.

The symmetrically or asymmetrically constructed guide system may be structured as a roller system with ~~an upstream~~ a deceleration module disposed above it for adjusting the ion influx energy, and it may consist of a ~~take-up~~ roller dispensing the film at the beginning of the processing path, a take-up roller for the irradiated carrier ~~foil~~ film at the end of the processing path, two ~~fixing~~ guide rollers each moved inwardly towards the center and disposed above the plane of ~~feed~~ the dispensing and take-up rollers and a deflection ~~rollers~~ roller preferably positioned in the middle between the ~~fixing~~ guide rollers. For adjusting the influx angle $+\alpha_1/-\alpha_2$ of the ion beams ~~onto~~ relative to the carrier ~~foil~~ film the deflection roller is arranged for vertical adjustment along an area of the axis of symmetry or parallel to the axis of symmetry of the roller system. For different influx angles $+\alpha_1/-\alpha_2$ the deceleration module may be used such that for each particular influx angle (e.g. for $+\alpha_1$ or for $-\alpha_2$) a corresponding value of influx energy of the penetrating ions may be set by constructing the module ~~of partial components~~

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from component parts of deceleration foils of different thicknesses. In a particular embodiment the deceleration module, over its longitudinal extent, is provided with foils of different thickness in order to ensure a desired influx value of the ions penetrating into the carrier material (2) for each influx angle $+\alpha_1$ or $-\alpha_2$.

The deflection roller ~~is~~ can be vertically adjusted, for instance, by its guidance on a rail.

~~For a more detailed explanation of the invention, reference may be had to the patent claims.~~

~~Details, characteristics and advantages of the invention will become apparent from the ensuing specification of embodiments. In the appurtenant drawings:~~:

DESCRIPTION OF THE SEVERAL DRAWINGS.

The novel features which are considered to be characteristic of the invention are set forth with particularity in the appended claims. The invention itself, however, in respect of its structure, construction and lay-out, as well as manufacturing techniques, together with other objects and advantages thereof, will be best understood from the following description when read with reference to the drawings, in which:--

Fig. 1 is a schematic presentation of possible common intersections of recesses in ion trace ~~foils~~ films;

Fig. 2 depicts a variant of an embodiment of the method in accordance with the invention with collimation of the high-energy heavy ions;

Fig. 3 is a representation of the course of the connection strength ~~of such~~

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~~composite components as an~~ between the ion trace ~~foil~~ film and copper components of the composite as a function of ~~pore~~ the diameter of the pores in the ion trace ~~foil~~ film;

Fig. 4 depicts the schematic structure of an arrangement with a deceleration module for practicing the irradiation process of a ~~foil~~ film;

Fig. 5 is a plan view of an electron-microscope image of a typical profile of a strongly fissured surface with a strong depth relief in a polyester ion trace ~~foil~~ film.

Fig. 1 depicts the creation of common intersections of recesses 4 in ion trace ~~foils~~ films 2. Fig. 1.1 is a sectional view through a carrier ~~foil~~ film 2 with two coinciding pairs 4.1 which contribute significantly to the connection strength and one coinciding pair which contributes little to the connection strength. Fig. 1.2 additionally shows a spatial representation of an intersection 4.1 with recesses (pores) 4.3.

Fig. 2 is a schematic view of an advantageous variant for practicing the method in accordance with the invention with collimation of the high-energy heavy ion beams I for producing as large a number of common intersections 4 of recesses as possible in ion trace ~~foils~~ films 2. A common intersection 4 connotes the coinciding or crossing of two recesses.

Fig. 2.1 schematically depicts an irradiation mask 5. The ~~foil~~ film 2 unwound from and wound on rolls 6 and 7 is passed twice under the mask 5; the ions 1.2 are beamed during each passing of the ~~foil~~ film at a bombardment
angle $\pm\alpha$.

Fig, 2.2 schematically depicts, in relation to an intersection, the ion trajectories 1.1 permeating the mask 5 and penetrating into the solid material

2. As a result of this method step latent ion traces 3 are generated prior to the subsequent etching process. The subject matter of Fig. 2.3 is the schematic presentation of the creation of intersections in a sectional plane. What is shown is the common intersection 4 of recesses (pores) after the etching process.

Fig. 3 depicts the graphic evaluation of ~~an~~ a connection strength test of composites consisting of ion trace ~~foils~~ films 2 (polyimide) and copper as a function of ~~pore~~ the diameter of the pores in the ion trace ~~foil~~ film. The pulling-off or stripping test was performed immediately after removal of the samples from an aqueous solution.

In order to explain the effect of common intersections on the connection strength of a composite consisting of two components the relative porosity, i.e. the ratio of the etched to the non-etched surface, may be taken as a measure of the effectiveness of the method of forming the surface-depth-relief. The following ~~is~~ holds true for a constant ion fluence: the greater the porosity the greater the number of common intersections and, hence, of the connection strength. Since at an increasing porosity the diameter of the recesses also increases, the probability of the formation of common intersections increases as well. However, at a very great porosity, generated by strong overetching, ~~one may observe a reduction of~~ the connection strength is reduced since overetching results in the destruction of recesses. At the same time, an increase in pore diameter leads to a reduced aspect ratio and to a reduction in the proportion of the solid material in the volume segment of the carrier ~~foil~~ film material. That, too, causes a deterioration in the value of the connection strength. On the basis of these counter-acting effects, the resultant maximum in the connection strength curve ~~depending upon~~ relative to the porosity is as shown in Fig. 3.

Fig. 4 schematically depicts an arrangement with a deceleration module for executing the operation of irradiating a polyester ~~foil~~ film to be

used as the carrier ~~foil~~ film of a flexible circuit board.

In a first example of ~~application~~ use, an ion trace ~~foil~~ film 2 is processed as a carrier ~~foil~~ film of a semi-rigid layer of copper for use as a starter material for flexible circuit boards.

As shown in Fig. 4, a ~~foil~~ film 2 of a thickness of 50μm consisting of polyethylene terephthalate (PETP, a so-called polyester) is subjected to irradiation by an $^{84}Kr^{+}$(krypton)-ion beam 1. For this purpose, the starter material provided in a roll (width 50 cm) is moved through the bundle of ion rays I over a roller system consisting of five rollers. ~~Upstream of~~ Above the roller system 6, 7, 8, 9, 10, 12 there is provided, in the direction of propagation of the heavy ion beam 1.1, a deceleration module 13, which is arranged orthogonally relative to the direction of propagation of the ion beam 1.1, ~~ahead of~~ above the roller system 6, 7, 8, 9, 10, 12, and which is permeated by the bundle of rays 1 and which determines the influx energy of the ions into the ~~foil~~ film material. The roller system which in this case is structured symmetrically, consists of a feed roller 6 for the polyester ~~foil~~ film 2 and a take-up roller 7 for the polyester ~~foil~~ film 2 ~~followings it~~ following its irradiation. Between these rollers, there are provided a first ~~fixing~~ guide roller 8, a deflection roller 9 as well as a second ~~fixing~~ guide roller 10. The bundle of ion rays 1 sweeps the area between the two ~~fixing~~ guide rollers 8 and 10, an aperture or diaphragm 11 being provided for selectively blocking any partial section of the bundle of ion rays 1. The deflection roller 9 is mounted on a rail 12 for sliding movement parallel to the direction of the bundle of ion rays 1 and thus allows to vary the influx angle a of the ions between -70°and + 70°relative to the a line extending normal to the surface.

In the present embodiment, the influx angle is set at 45°. The partial area in which the deflection roller 9 is positioned is blocked out of the bundle of ion rays 1. Thus, there are only two effective partial beam portions with which the influx angles -45°and +45°be associated. Within the mentioned

angles they generate two families of latent ion traces 3. The total irradiation density (fluence) amounts to 5.10^7 m^2.

The influx energy of the ions is 1.2 MeV/am which leads to an average range of 20 µm.

The irradiated ~~foils~~ films 2 are then subjected to etching with a 3 molar NaOH solution for 10 to 30 minutes at a temperature of 80 °C. The result of the etching is opening of the latent ion traces 3 to cylindrical closed-bottom recesses of 2 µm diameter and a depth of about 18 to 19 µm. This length is somewhat less than the depth of penetration of the ions since at the end of the ion trace the transfer of energy to the polyester ~~foil~~ film 11 becomes so small that the trace cannot be etched. The length of the section which cannot be etched amounts to about 5 to 10 of the entire length of the ion trace.

To fabricate the functional layer, a starter layer of a thickness of .2 to .4 µm and consisting of copper is applied by sputtering (vacuum deposition). The copper layer proper of a thickness of 5 to 140 µm is afterwards galvanically precipitated. The copper-coated polyester ~~foil~~ film thus fabricated is characterized by a high connection strength of the cover layer (> 2 N/m) established by it mechanical anchoring in the pores of the base material. It is very suitable for use as a flexible circuit board for high mechanical alternating stresses.

In a second embodiment, an ion trace ~~foil~~ film is processed with a high specific surface for supporting an aluminum coating.

A polyester ~~foil~~ film 2 consisting of polyethylene terephthalate (PETP) of a thickness of 23 µm is subject to irradiation by $^{40}Ar^{*}$-ions 1. For this purpose, the rolled starter material (width 50 cm) is fed over the roller system 7 -10 described in connection with the first embodiment. In this case, the influx angle a is set at ±30°, i.e. irradiation is successively carried out within

angles +30° and -30° relative to a line extending normal to the surface of the ~~foil~~ film 2. The radiation density is 5•10~ cm^2. The influx energy of the ions is set at .11 MeV/amu by the deceleration module. This results in latent ion traces the effective (etchable) length of which is about 7 µm.

The surface of the irradiated ~~foil~~ film 2 is then subjected to etching for 6 to 8 minutes at a temperature of 90 °C in a 5-molar NaOH solution causing the latent ion traces 3 to be opened to frusto-conical cavities or closed-bottom recesses of a depth of about 7 µm resulting from the above-mentioned effective length. The diameter of the (because of the steep angle of bombardment) almost circular openings of the recesses at the surface is 1.9 to 2 µm which corresponds to a surface of about 3 $\mu m^2 = 3 \cdot 10^{-8}$ cm^2. The total surface area covered by recesses being the product of recess surface and total irradiation density, thus is about 1.5 cm^2 per surface unit of 1 cm^2 and, therefore, corresponds to a theoretical surface proportion of about 150%. The etching process is thus continued in this case until the surface covered by recesses mathematically exceeds the available surface by about 50. The process is called overetching and is characterized by ~~strong~~ significant overlapping of the recesses. The result of this formation is a ~~foil~~ film with a strongly fissured surface and a pronounced depth relief. A typical example is shown in Fig. 5. The ~~foil~~ film has an extremely high specific surface. Its mechanical stability is maintained since the thickness of the structured area amounts to only about one third of its total thickness.

The ~~foil~~ film structured in this manner is subjected to aluminum vapor deposition at a working pressure of □ $1 \cdot 10^{-1}$ mbar. The vapor deposition time required to yield a particular layer thickness has to be determined experimentally. In contrast to conventional Al-coated ~~foils~~ films, the Al layer thus precipitated is not only adhesively bonded to the substrate but is additionally mechanically anchored in the recesses thereof.

Many practical applications of such Al-coated polymeric ~~foils~~ films

require subsequent oxidation which generate mechanical stresses in theAl_2O_3-Al_xO_y- Al polymer layer system. (Al_xO_y is a non-stoichiometric transition layer between the metal and the oxide which is characterized by a continuous change in the oxygen content.) The system consisting of the oxide, transition layer and metal is of great connection strength; but the mechanical stresses are transmitted to the metal and polymer composite. In conventionally coated ~~foils~~ films this ~~what~~ would result in flaking of the layer off the substrate (polymer). Based on the mechanical anchoring realized by the invention, the connecting strength of the layer is improved so much that flaking as a result of surface oxidation is prevented. Similarly, the flexibility of the product is improved so that it may be wound up as a roll with a very small internal bending ~~ration~~ ratio.

Such ~~foils~~ films with aluminum vapor deposition and ~~having~~ provided with an oxidized surface may be used as starter materials for the production of electrolytic capacitors.

What is claimed is: